

structure in the density of states associated with symmetry points on the surface of the Brillouin zone is absent in the amorphous-film results. Using the above results—the change in the valence- and conduction-band density of states and the change in optical selection rules—one can account for the observed changes in the optical properties as one goes from crystalline to amorphous germanium.

In the following Letter Herman and Van Dyke examine through a band calculation the effect of changing the Ge lattice constant from that of crystalline Ge to the average value of amorphous Ge. Combining this with the photoemission results, some insight can be obtained into the separate effects of lattice spacing and disorder.

The authors are grateful to Dr. Frank Herman and Dr. A. Bienenstock for helpful discussions.

---

\*Work supported by Advanced Research Projects Agency through the Center for Materials Science at Stanford University, Stanford, Calif.

†Permanent address: Naval Weapons Center, China Lake, Calif.

<sup>1</sup>J. Tauc et al., in Proceedings of the International Conference on Physics of Noncrystalline Solids, Delft, The Netherlands, 1964 (North-Holland Publishing Company, Amsterdam, 1965), p. 606.

<sup>2</sup>T. M. Donovan, E. J. Ashley, and H. E. Bennett, *J. Opt. Soc. Am.* **53**, 1403 (1963).

<sup>3</sup>H. R. Philipp and E. A. Taft, *Phys. Rev.* **113**, 1002 (1959).

<sup>4</sup>H. R. Philipp and H. Ehrenreich, *Phys. Rev.* **129**, 1550 (1963).

<sup>5</sup>F. Herman, R. L. Kortum, and C. D. Kuglin, *Intern. J. Quantum Chem.* **1S**, 533 (1967).

<sup>6</sup>M. L. Cohen and T. K. Bergstresser, *Phys. Rev.* **141**, 789 (1966).

<sup>7</sup>F. G. Allen and G. W. Gobeli, *Phys. Rev.* **144**, 558 (1966).

<sup>8</sup>W. E. Spicer and C. N. Berglund, *Rev. Sci. Instr.* **35**, 1665 (1964).

<sup>9</sup>W. E. Spicer and R. C. Eden, in Proceedings of the Ninth International Conference on the Physics of Semiconductors, Moscow, U. S. S. R., July, 1968 (to be published).

<sup>10</sup>J. L. Shay and W. E. Spicer, *Phys. Rev.* **161**, 799 (1967).

<sup>11</sup>F. Herman, R. L. Kortum, C. D. Kuglin, and J. L. Shay, in Proceedings of the International Conference on II-VI Semiconducting Compounds, Providence, 1967 (W. A. Benjamin, Inc., New York, 1967), pp. 271-289.

---

## NEW INTERPRETATION OF THE ELECTRONIC STRUCTURE AND OPTICAL SPECTRUM OF AMORPHOUS GERMANIUM\*

Frank Herman and John P. Van Dyke  
Lockheed Palo Alto Research Laboratory, Palo Alto, California  
(Received 28 October 1968)

The electronic density of states of amorphous germanium is simulated by that of a dilated germanium crystal having the same density as amorphous germanium (3.9 g/cm<sup>3</sup>). This simulated density of states accounts quite nicely for some recent experimental results obtained by optical and photoemission techniques. The band structure and density of states of a suitable dilated germanium crystal may well be a better starting point for a more sophisticated analysis of the electronic structure of amorphous germanium than their counterparts in normal crystalline germanium.

Donovan and Spicer<sup>1</sup> have recently investigated the electronic structure of amorphous films of germanium using the highly successful photoemission technique.<sup>2</sup> Their experimental results indicate that the valence- and conduction-band density of states is considerably different in amorphous and crystalline germanium. These experimental findings stand in sharp contrast to earlier theoretical discussions of amorphous semiconductors,<sup>3,4</sup> in which the density of states of a disordered crystalline material is usually regarded as merely a slightly perturbed version

of the density of states of the corresponding ordered crystalline material. Although these theoretical discussions emphasize the role played by the atomic disorder in fuzzing out the electronic density of states, particularly in the neighborhood of the band edges (band tailing effects), they usually ignore the important changes in electronic structure that can be produced by disorder-induced changes in the average atomic density (average number of atoms per unit volume).

In this Letter we will introduce a simple model

for the electronic structure of amorphous germanium which enables us to estimate the changes just mentioned. Our model accounts quite nicely for Donovan and Spicer's observation that the maximum in the valence-band density of states in amorphous germanium is about 1.5 eV closer to the top of the valence band than in crystalline germanium. Combining our electronic structure model with Donovan and Spicer's nondirect constant-matrix-elements model for interband optical transitions, we can account for the fact that the principal maximum in the experimental reflectivity spectrum of amorphous germanium<sup>4,5</sup> lies at a considerably lower energy than its counterpart in crystalline germanium.

Although the detailed atomic arrangement in amorphous germanium is not fully understood,<sup>6,7</sup> it is known experimentally<sup>8</sup> that the density of amorphous germanium is  $3.9 \pm 0.4$  g/cm<sup>3</sup>, which is about 28% less than the crystalline value of 5.35 g/cm<sup>3</sup>. Even though the first- and second-order neighbor distances in amorphous germanium may indeed be quite close to those in crystalline germanium, the lower atomic density in the former may be readily understood in terms of the inefficient packing of atoms associated with the disorder.

For the purposes of discussion, we will temporarily ignore the disordered atomic arrangement in amorphous germanium, and concentrate our attention on the fact that the average atomic density is considerably less in amorphous than in crystalline germanium. We will make the rather bold assumption that the electronic density of states in amorphous germanium can be simulated (at least to a first approximation) by the density of states of a dilated germanium crystal having the same density as amorphous germanium (3.9 g/cm<sup>3</sup>).

In an earlier publication,<sup>9</sup> we calculated the lattice-constant dependence of the energy-band structure of crystalline germanium. The most important results of this earlier work are reproduced in Fig. 1. The band structure at  $\Gamma$ , X, and L for a dilated germanium crystal having a density of 3.9 g/cm<sup>3</sup> can be read off Fig. 1 by setting  $a/a_0 = 1.11$ . We have obtained the band structure throughout the reduced zone and the density of states of such a dilated germanium crystal by fitting a pseudopotential-type interpolation scheme<sup>10</sup> to the energy levels at  $\Gamma$ , X, and L in Fig. 1 for  $a/a_0 = 1.11$ . These theoretical results for dilated germanium are shown in Fig. 2. The band structure of dilated germanium is

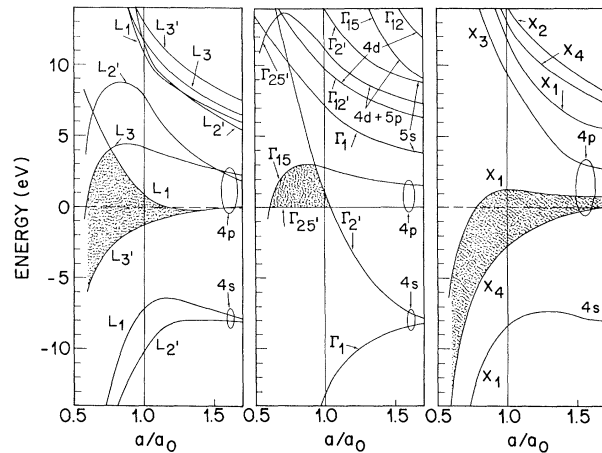


FIG. 1. Energy-band structure of crystalline germanium as a function of lattice constant at three key points in the reduced zone. The lattice constant of normal germanium is denoted by  $a_0$ . The zero of energy is placed at the top of the valence band ( $\Gamma_{25'}$ ). For further details, see Ref. 9.

seen to be an exaggerated version of the Groves-Paul model for grey tin.<sup>11</sup> Note that dilated germanium is actually a semimetal with zero thermal gap rather than a semiconductor. Also shown for comparison in Fig. 2 is the density of states of normal ( $a/a_0 = 1$ ) crystalline germanium, as reported in an earlier publication.<sup>12</sup>

It is already clear from Fig. 1 that the width of the uppermost valence band becomes smaller as the lattice constant becomes larger. The consequences of this are seen in greater detail in Fig. 2(b). For example, we see that the principal maximum in the valence-band density of states shifts by about 1 eV to higher energies (the zero of energy is held fixed at the top of the valence band). The secondary maximum and the trailing edge also shift to higher energies by

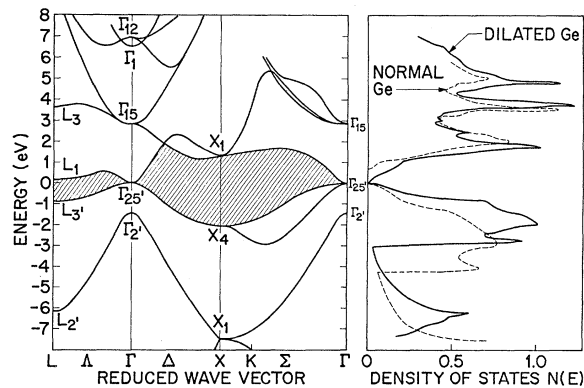


FIG. 2. (a) Energy band structure of dilated germanium ( $a/a_0 = 1.11$ ). (b) Density of states of normal ( $a/a_0 = 1$ ) and dilated ( $a/a_0 = 1.11$ ) germanium.

about 1.3 eV. To the extent that our dilated germanium crystal simulates amorphous germanium, the above results are consistent with Donovan and Spicer's observation<sup>1</sup> that the uppermost valence bands in amorphous germanium are narrower than those in crystalline germanium. In fact, the principal maximum in  $N(E)$  in Fig. 2(b) lies just 2 eV below the top of the valence band, in reasonable agreement with Donovan and Spicer's result.

Since we have neglected the actual atomic disorder in amorphous germanium, as well as the fact that first- and second-order neighbors probably have almost identical separations in amorphous and (normal) crystalline germanium, our electronic structure model for amorphous germanium is obviously only a first approximation. In higher approximations, we might expect the sharp structure in the conduction-band density of states to be washed out (as the results of Donovan and Spicer suggest), and the density of states in the lower reaches of the conduction band to be considerably less than is suggested by Fig. 2 (so that amorphous germanium would be more nearly a semiconductor with fuzzy band edges than a clearcut semimetal).

Turning next to the optical spectrum, we show in Fig. 3(a) the experimental  $\epsilon_2$  curve for amorphous germanium,<sup>4,5</sup> as well as the corresponding theoretical  $\epsilon_2$  curve based on (a) the band structure shown in Fig. 2(a), and (b) the nondirect constant-matrix-element optical transition

model of Donovan and Spicer.<sup>1</sup> (The latter curve was kindly provided by Donovan who obtained it using our density-of-states information.) For purposes of contrast, we show in Fig. 3(b) the theoretical  $\epsilon_2$  curves for normal ( $a/a_0 = 1$ ) and dilated ( $a/a_0 = 1.11$ ) germanium based on (a) the band structure shown in Ref. 12 and Fig. 2(a); (b) the conventional direct (vertical interband) transition model<sup>12</sup>; and (c) pseudopotential-type matrix elements.<sup>12</sup> (The experimental  $\epsilon_2$  curve and the theoretical  $\epsilon_2$  curve based on constant matrix elements for normal germanium can be found in Ref. 12.)

It is clear from Fig. 3(a) that the experimental  $\epsilon_2$  curve for amorphous germanium bears a striking similarity to that calculated for dilated germanium in terms of the nondirect transition model. Considering the crudeness of the constant-matrix-element assumption (which was used in this calculation), the agreement between theory and experiment is quite remarkable. At the same time, the experimental  $\epsilon_2$  curve for amorphous germanium is quite different from the theoretical  $\epsilon_2$  curves for normal or dilated germanium based on the direct-transition model.

The agreement between theory and experiment manifest in Fig. 3(a) would be destroyed if the nondirect-transition model were used, but the change in band structure associated with the change in atomic density were ignored. A nondirect optical-transition calculation based on the density of states of normal germanium (see Ref. 1) would lead to an  $\epsilon_2$  curve which peaks at about 4.5 eV, rather than at about 2.7 eV [as in Fig. 3(a)]. In the present application to amorphous germanium, the nondirect-transition model appears to be considerably more successful than the direct-transition model in accounting for all of the photoemission and most of the optical results.<sup>13</sup> Presumably, this is a consequence of the long-range disorder in amorphous germanium.

Although some of the details of Fig. 2(a) would undoubtedly change if the actual first- and second-order neighbor positions and the overall disorder in amorphous germanium were properly taken into account, we believe that the idealized band structure shown in Fig. 2(a) may well be a better starting point for a more sophisticated analysis than the band structure of normal crystalline germanium. In any event, we believe we have taken an important step in the direction of understanding the electronic structure and optical spectrum of amorphous germanium by taking

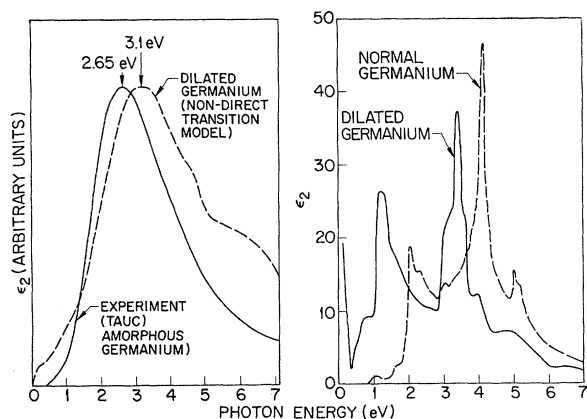


FIG. 3. (a) Comparison of experimental  $\epsilon_2$  curve for amorphous germanium Refs. 4 and 5 and theoretical  $\epsilon_2$  curve based on the band structure of Fig. 2(a) and the nondirect constant-matrix-element optical transition model (Ref. 1). (b) Comparison of theoretical  $\epsilon_2$  curves for normal and dilated germanium based on direct optical transition model (pseudopotential type matrix elements).

the density variation of the band structure into account.

The present theoretical study was motivated by Donovan and Spicer's striking experimental results.<sup>1</sup> The authors are grateful to Mr. T. L. Donovan and Professor W. E. Spicer for bringing these results to their attention, and for many stimulating discussions.

---

\*Research supported in part by the Lockheed Independent Research Fund; in part by the Air Force Cambridge Research Laboratories, Office of Aerospace Research, under Contract No. AF 19(628)-5750; and in part by the Aerospace Research Laboratories, Office of Aerospace Research, under Contract No. AF 33(615)-5072.

<sup>1</sup>T. M. Donovan and W. E. Spicer, preceding Letter [Phys. Rev. Letters 21, 1572 (1968)].

<sup>2</sup>W. E. Spicer and R. C. Eden, in Proceedings of the Ninth International Conference on the Physics of Semiconductors, Moscow, U.S.S.R., 1968 (to be published). This paper contains an extensive list of references to photoemission experiments.

<sup>3</sup>A. I. Gubanov, Quantum Electron Theory of Amorphous Conductors (Consultants Bureau, New York, 1965).

<sup>4</sup>J. Tauc, in "Optical Properties of Solids," edited by F. Abeles (North-Holland Publishing Co., Amsterdam, The Netherlands, to be published). See also J. Tauc, Materials Res. Bull. 3, 13 (1968).

<sup>5</sup>J. Tauc, A. Abraham, L. Pajasova, R. Grigorovici, and A. Vancu, in Proceedings of the Conference on Noncrystalline Solids, Delft, The Netherlands, 1964 (North-Holland Publishing Co., Amsterdam, The Netherlands, 1965), p. 606. See also J. Tauc and A. Abraham, to be published.

<sup>6</sup>H. Richter and G. Breitling, Z. Naturforsch. 13a, 988 (1958).

<sup>7</sup>R. Grigorovici, Materials Res. Bull. 3, 13 (1968).

<sup>8</sup>A. H. Clark, Phys. Rev. 154, 750 (1967).

<sup>9</sup>F. Herman, R. L. Kortum, C. D. Kuglin, and R. A. Short, in Quantum Theory of Atoms, Molecules, and the Solid State, edited by P. O. Löwdin (Academic Press, Inc., New York, 1966), p. 381. See also F. Herman, R. L. Kortum, C. D. Kuglin, and R. A. Short, J. Phys. Soc. Japan Suppl. 21, 7 (1966).

<sup>10</sup>The pseudopotential coefficients used in constructing Fig. 2 are as follows:  $v(111) = -0.2497$ ,  $v(220) = 0.0145$ , and  $v(311) = 0.0115$  (Rydberg units). Also,  $(m^*)^{-1} = 0.9924$ . See F. Herman, R. L. Kortum, C. D. Kuglin, and J. L. Shay, in Proceedings of the International Conference on II-VI Semiconducting Compounds, Providence, Rhode Island, 1967, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1967), p. 503, for further details concerning the analogous calculation for normal ( $a/a_0 = 1$ ) germanium.

<sup>11</sup>S. Groves and W. Paul, in Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964 (Dunod, Paris, France, 1964), p. 41.

<sup>12</sup>Herman, Kortum, Kuglin, and Shay, Ref. 10.

<sup>13</sup>On the other hand, the broad maximum in the photoconductivity spectrum of amorphous germanium observed at 1.1 to 1.2 eV by Grigorovici (Ref. 7) over a wide temperature range [and at 1.5 eV by Clark (Ref. 8) at 4.2°K] may possibly be related to the  $\Lambda$ -type transitions that are responsible for the 1.2 eV peak in the direct transition  $\epsilon_2$  calculation for dilated germanium [cf. Fig. 3(a)]. If so, the lower energy optical transitions would be better described by the direct-transition model, and the higher energy transitions by the nondirect-transition model.

---

## CRITICAL OPALESCENCE IN QUARTZ\*

S. M. Shapiro and H. Z. Cummins

Department of Physics, The Johns Hopkins University, Baltimore, Maryland 21218

(Received 3 October 1968)

The intense scattering of light by quartz in the vicinity of the  $\alpha$ - $\beta$  transition, first observed by Iakovlev and co-workers in 1955, has been studied by Raman and Brillouin spectroscopy and by visual observation. Our results indicate that the observed "opalescence" does not originate from critical fluctuations of the order parameter but is generated by essentially static domain walls separating microdomains of opposite electrical twins.

Crystalline quartz undergoes a transition at 573°C from the low-temperature  $\alpha$  phase (symmetry  $D_3$ ) to the high-temperature  $\beta$  phase (symmetry  $D_6$ ). The transition is marked by anomalies in many of the physical properties of quartz.<sup>1</sup> In 1956, Iakovlev, Velichkina, and Mikheeva observed that the scattering of Hg light by quartz

increases in the vicinity of the transition by  $\sim 10^4$  over the room-temperature level and that under white-light illumination, the scattering volume appears as a "fog zone."<sup>2</sup> They termed this phenomenon "critical opalescence" since it resembles the intense scattering observed in fluids near the critical point. Subsequently Ginzburg